INTERNAL OXIDATION
OF SILVER ALLOYS WITH TELLURIUM, SELENIUM AND SULPHUR

Silver alloys with tellurium, selenium and sulphur fulfil the conditions for the internal oxidation. Microstructure of these alloys consists of matrix (dilute solid solution) and particles of intermetallic compounds. Internal oxidation of ternary alloys is very similar to that of the binary alloys, but there are also distinctions in thermodynamics properties of alloying elements.

At the direct oxidation of the particles of the intermetallic compound the phenomena of the selective oxidation was observed. Concentration of more reactive elements is increasing in the oxidized part of the particles of the intermetallic compound (Te in AgTeSe alloys). Therefore the precipitated oxides formed with diffusional internal oxidation are richer with less reactive alloying element (Se in AgTeSe alloy). In the precipitated oxide particles the concentration of selenium is more than twice higher than of tellurium.

Key words: internal oxidation, silver, alloy, compound, particle

INTRODUCTION

Silver alloys with tellurium, selenium or sulphur fulfil the conditions for the internal oxidation [1], but the ternary alloys with two of these elements realize the conditions of the so-called selective internal oxidation, although the internal oxidation is selective itself [2, 3]. Gibbs free energies (Figure 1.) of the discussed elements [4] are one of the selectivity indicators, though they could be double or triple oxides at the internal oxidation, respectively [5].

Low alloyed binary and ternary silver alloys are two-phase with these elements. The microstructure of these alloys consists of the metal matrix, which is very diluted solid solution of the silver and the intermetallic compounds [6]. They are compounds of silver with the alloying element in the binary alloys, and the solid solutions of the binary compounds [e.g. Ag,(Te, Se) and Ag,(Te, S)] in the three-component alloys [7].

EXPERIMENTAL WORK AND DISCUSSION

For the experiments the three-component silver alloys in combination with two alloying elements of Te-Se, Te-S and Se-S were made, thus the concentrations of the alloying elements were equal, but the common one was 1,3 mol % [8].

Internal oxidation of two or multi-phase silver alloys was taking place on two ways [9]:
- by the direct oxidation of the particles of the intermetallic compounds, and
- by the diffusional oxidation of the alloying elements of the solid solution.
The products of the direct oxidation are essentially larger than the oxides, which were precipitated from the solid solution.

The oxidation was taking place between 750 and 830 °C, where the molten products were also formed, which mainly affected on the progress of the oxidation [10]. Such cases are frequently characterized as the catastrophic oxidation [11].

In the AgTeS alloy (Figures 3., 4.) the sulphur is the most reactive element, therefore it starts to oxidize first. The remaining part of the particles of the intermetallic phase is rich on the tellurium, since the sulphur oxides form the new gas phase.

After the completed direct oxidation of the particles of the Ag,(Te, S) intermetallic phase the minimal sulphur concentration or zero one in the oxide was observed respectively. But in the metal matrix the fine gas pores were not observed, which should indicate the formation of the sulphur oxides after the diffusional mechanism.
The same mechanism of the oxidation is taking place for the alloys with sulphur, but it differs for the AgTeSe alloys. At the direct oxidation of the AgTeSe alloys the tellurium oxidizes first and the non-oxidized part of the particles of the intermetallic compound becomes richer on the selenium, therefore the concentration and the activity of the selenium in the solid solution are increasing. Therefore one part of the selenium is dissolved in the silver phase, but on the contrary the activity of tellurium in the oxide is decreasing and part of it diffuses into the oxidized particle of the intermetallic phase. Thus the solid solution becomes richer on the selenium and poorer on the tellurium. Therefore the oxides formed by the direct oxidation are richer on tellurium, and those formed by the diffusional oxidation are richer on the selenium.

CONCLUSIONS

At both alloys the sulphur is the most reactive element, which oxidizes first at the direct oxidation. It creates the independent gaseous phase of its oxides and thus it is extracting from the particles of the intermetallic compound, which becomes richer either on the tellurium or on the selenium. Therefore the oxides formed by the direct oxidation are Ag$_2$SeO$_3$ or Ag$_2$TeO$_3$ and the gaseous pores of the sulphur oxides at the final stage of the oxidation. The diffusional formed oxides are not gaseous at the direct oxidation probably due to the sulphur oxidation from the solid solution on the large gaseous pores.

That explanation is supported by the relatively high diffusional rate of the sulphur in the silver phase and by the high energy, which is needed for the creation of the gaseous pores in the solid metal matrix.

REFERENCES